# Singular droplets

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<u>Summary</u> We study droplets of complex fluids, having either surfactants or polymers dissolved in the fluid. We study the spreading at low Reynolds number. It turns out that both polymers and surfactants slow down the spreading. A special type of surfactants (trisiloxanes), however, leads to "superspreading", in which the droplet spreads out orders of magnitude quicker than with usual surfactants. We provide quantitative explanations for the slowing down of the spreading; however, the mechanism of the speeding up remains a puzzle. At high Reynolds number, we study the impact and subsequent retraction of aqueous droplets on hydrophobic surfaces. Here, the polymer and surfactant additives slow down the retraction, leading to improved deposition. The mechanisms are however very different: the surfactants act on the surface tension, whereas the polymers change the bulk rheology.

#### 1. Introduction

Drops spreading over solid surfaces represent a basic phenomenon important to a wide variety of coating and deposition processes. Efficient deposition is critical to most painting, coating and solution delivery applications. The obvious solution to improve deposition is to add surface-active agents to the droplets to improve the spreading ability of the solutions. However, a full quantitative understanding of the influence of surfactant addition on the spreading dynamics is still lacking. In addition, one can modify the bulk rheology by adding polymers. We study here the deposition of surfactant- and polymer-lader liquids, and see how these additives modify the droplet dynamics both at low and high Reynolds number.

# 2. Low Reynolds number: spreading of droplets

### 2.1 Spreading with surfactants

We study the spreading of aqueous surfactant solutions drops onto a hydrophobic surface. The addition of small amounts of trisiloxane surfactants leads to a very rapid 'super'-spreading of the droplets, faster than that of a simple liquid with the same surface tension and viscosity. On the other hand, classical surfactants are shown to slow down the spreading relative to that of the reference system without surfactants. The latter is linked to the dynamic surface tension of the solutions. For the superspreading surfactant, Marangoni effects are suggested to provide a supplementary different driving force for the spreading that leads to the fast dynamics.

### 2.1 Spreading with polymers

We study the spreading of aqueous droplets on a hydrophilic surface in two different dilute or semidilute polymer solutions. The different solutions exhibit only a single non-Newtonian property, in the sense that other non-Newtonian effects can be neglected. Solutions of stiff polymers have a strong shear rate dependence of the viscosity. Relative to Newtonian fluids the spreading is slowed down For solutions of flexible polymers, elastic effects such as normal stresses are dominant, whereas the shear viscosity is almost constant. Again, a slower spreading is found in this case. We characterize the non-Newtonian flow properties of these polymer solutions completely, allowing for separate and quantitative investigation of the influence of the two most common non-Newtonian properties on the spreading of droplets

## 3. High Reynolds number: impact and retraction

### 3.1 Polymers

Drops impacting onto solid surfaces are important for many applications. An important example being the treatment of plants with herbicides and pesticides, which require precise targeting to meet stringent toxicological regulations. However, the outer wax-like layer of the plant produces a non-wetting interface that causes sprayed droplets to rebound off the foliar surfaces. The plant retains often less than 50% of the initial spray. Our study focuses on the impact and subsequent retraction of non-wetting aqueous drops onto a hydrophobic surface, for which rebound of the droplets limits their deposition. Although extensive experimental and theoretical work has been dedicated to this phenomenon, non-Newtonian rheological effects have not been considered in any detail. Here we show that by adding very small amounts of a flexible polymer to the aqueous phase, we are able to inhibit droplet rebound and dramatically improve deposition without significantly altering the shear viscosity of the solutions. Instead, the results can be understood by taking into account the non-Newtonian elongational viscosity, high values of which provide resistance to drop retraction after impact, that in turn prevent droplet-rebound.

#### 3.2 Surfactants

The behaviour of surfactant-laden droplets turns out to be remarkably similar to that of the polymers: the retraction is almost completely suppressed, and therefore droplet rebound also. The mechanism of the slowing down is however very different: for the surfactants the driving force of the retraction, the surface tension of the liquid-vapour interface, is much smaller. This becomes evident when solutions with different dynamic surface tensions are studied: if the surfactant molecules arrive too slowly at the free surface, rebound may still occur.

#### References

- [1] S. Rafaï, A. Boudaoud, D. Bonn, *Spreading of non-Newtonian fluids on hydrophilic surfaces*, J. Fluid Mech., **513**, 77 (2004)
- [2] V. Bergeron, D. Bonn, J.-Y. Martin, L. Vovelle "Impact and retraction of viscoelastic drops" Nature, **405**, 772 (2000)